

Influence of some nanostructured materials additives on the performance of lead acid battery negative electrodes



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ABSTRACT

Various nanostructured materials, namely, multi-walled carbon nanotube (MWNT), graphene, Vulcan XC-72 carbon, lead oxide nanorods and ball milled lead oxide nanospheres have been incorporated as additives in the negative paste mix of lead acid battery negative electrodes. Charge/discharge cycling has been performed at room temperature on 9 Ah cells with 2 (+) ve/1 (–) ve cells assembled from these negative electrodes and their performances have been compared. It has been noticed that the graphene and MWNT additives introduced negative electrodes give 11 and 12% improved specific capacity and active material utilization (a.m.u), respectively, than those of the electrodes without additive. The reasons for this improvement is attributed to integration of these additives into the skeleton structure of the negative active mass of the electrodes that forms uniform rectangular beads of size < 200 nm during the course of charge/discharge cycling.

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1. Introduction

Though many new battery technologies are emerging in the present days, the demand for the century old lead acid battery technology is also continuously increasing and it can compete with other batteries in modern times. In fact, there is going to be a high demand for this technology in future applications which include stationary, and start–stop vehicles which turn off their engines and restart them at traffic and stop signs as a means of reducing fuel cell consumption. However, lead acid battery technology is still not free from problems. It suffers from many problems and one of them is negative plate sulfation accompanied by decrease in battery capacity and cycle life [1–6].

The problem of improper utilization of the active materials is present in both positive and negative electrodes. Several authors have tried to add various types of carbon to the negative active mass (NAM) and have come out with the inference that the active material utilization (a.m.u) could be improved with the incorporation of the carbon additives [7–14]. In this work, we have attempted to increase the a.m.u of the negative electrode materials by introducing some nanostructured materials in the NAM. This exercise has been carried out on 9 Ah negative electrodes (140 mm × 120 mm × 1.9 mm) belonging to automobiles and

uninterrupted power supply batteries rather than carrying out on small laboratory size electrodes (such as $C_n \approx 0.1$ Ah) so that the outcome of the investigation will be useful to the batteries manufacturers without having to go through too much of industrial R&D trials. Nanomaterials such as multi-walled carbon nanotube (MWNT), graphene, Vulcan XC-72 carbon, lead oxide nanorods and ball milled lead oxide nanospheres have been added in some weight percentages in the negative paste mix during the grid pasting phase of electrodes fabrication and their capabilities for increasing the a.m.u have been determined. Charge/discharge performances of these electrodes have been examined and the results indicated that the specific capacity and the a.m.u values have improved on incorporating various nanomaterials. Maximum improvement has been noticed for the MWNT additive. Morphologies of the additives added negative plates have been recorded using scanning electron microscopy (SEM) and it has been observed that the MWNT and graphene added negative plates form bead shaped crystals with sizes lying below 200 nm. It is suggested that the formation of small crystals has greatly helped to improve the performances of the negative electrodes. This idea of employing active materials in nano form and/or adding CNT/graphene as additive materials in the electrodes has been exploited extensively in the case of Li ion batteries [15–17]; whereas it has not been examined much in the case of lead acid battery. One of the objectives of the present investigation is also to fill up this gap and initiate a study on nanomaterials included large size lead acid battery negative plates.

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2. Experimental

2.1. Materials

The details of the nanomaterials additives incorporated in the negative paste mix and their weight percentages are shown in Table 1.

Since it has been noticed by Pavlov et al. [12] that carbon addition to the negative paste mix in quantities from 0.2 wt% to 0.5 wt% can give highest performances, we added an average quantity of 0.33 wt% carbon based nanomaterials in the negative paste mix used for making our electrodes. When lead oxide nanorods and lead oxide spherical particles were incorporated as additives, the quantities of the additives were maintained at 10 wt % and 45 wt%, respectively. These quantities have been concluded after carrying out a series of iterative exercises with different quantities of additives in different test cells until maximum improvement for the particular additive has been achieved.

The lead oxide required for preparing the negative electrodes has been procured from M/s Indian Oxide Ltd.

MWNT (purity: >94.5%) and graphene (purity: >83.28%) materials have been purchased from M/s Quantum Materials Ltd., Bangalore. Transition metal impurities present in MWNT was removed by refluxing with piranha solution (3:1 ratio of H₂SO₄ and HNO₃) at 60 °C for 7 hrs. The resulting MWNT was washed and dried. The graphene material was purified by refluxing with distilled water at 60 °C for the same period without subjecting to harsh chemical treatments. After cooling to room temperature, the residue (which might contain impurity metal hydroxides) was discarded. The supernatant solution containing pure graphene was taken and centrifuged. The solid residue containing pure graphene from this was taken and dried. The morphologies of the impure and purified MWNT and graphene materials have been characterized using High Resolution Transmission Electron Microscopy (HRTEM).

Fullerene obtained from M/s Sigma Aldrich (99.99% pure) was directly used as additive in the negative paste mix. Vulcan XC 72 has been obtained from M/s Cabot Corporation, USA.

The required lead oxide nanorod additive has been prepared in this laboratory using the following procedure [18,19]. 1 M NaOH solution was added drop wise to 0.015 M lead nitrate solution until pH 14 is attained. 3 mmol of cetyl trimethyl ammonium bromide (CTAB) was added to the above solution at 50 °C under magnetic stirring condition until complete dissolution of CTAB occurred. 1.5 M NaOCl was added to the above mixture. The resultant mixture was maintained at 85–100 °C for 3 h which resulted into a black brown product. It was washed several times using absolute ethanol, distilled water, centrifuged and dried at room temperature for 5 h.

Ball milled lead oxide additive has been prepared by milling red lead Pb₃O₄ powder (~ 50 μm) for 20 h in acetone medium at 300 rpm using tungsten carbide container and tungsten carbide balls in a Fritsch Pulvert-5 High Energy Planetary Ball mill [20].

The synthesized lead oxide and the ball milled oxide were characterized using XRD and HRTEM techniques.

Shimadzu XRD-600 equipment has been used for the XRD analysis and JEOL JEM 2100 (manufactured in Japan) has been used for recording the HRTEM images.

Table 1
Details of additives incorporated in the negative paste mix.

S. No	Additives	Weight percentage
1.	MWNT	0.33 wt%
2.	Graphene	0.33 wt%
3.	Fullerene	0.33 wt%
4.	Vulcan XC 72 carbon	0.33 wt%
5.	Lead oxide nano rods	10 wt%
6.	Ball milled lead oxide	45 wt%

The changes of porosity in some negative electrodes have been measured by liquid (glycerol) adsorption method. In this method, a non reactive glycerol (density, $d = 1.261 \text{ g/cm}^3$) is used to fill up the pores of small NAM pellets taken from the negative electrodes under vacuum. From the weight of the liquid hat entered into the pellet (ΔW), the volume has been estimated and subsequently the porosity of the materials has been estimated from the following relationship:

$$P(\%) = \frac{\Delta W}{d} \times \frac{1}{\text{volume}} \times 100$$

2.2. Electrochemical

The negative pastes have been prepared by mixing leady oxide with graphite (0.03 wt%), barium sulphate (0.5 wt%), lignin (0.35 wt %) and nanostructured additive materials along with dilute sulphuric acid in an electrical mortar assembly for an hour. The quantity of the leady oxide was 98.79 wt% when the carbon based nanostructured materials were used as the additives. It was 88.79 wt% and 53.79 wt% when lead oxide nano rod additives and lead oxide spheres were used as additives. The negative paste prepared without additives introduction had a wet density value 4.25 g/cm³. This value did not change much after the introduction of nanostructured carbon and lead oxide additives in the negative paste mix. Therefore, the effects of wet density on the microstructure changes of the electrodes are henceforth ruled out. The mix thus obtained were pasted on lead alloy grids of composition Pb-0.02%As-0.1%Sn-2%Sb-0.02%Se. All the pasted plates were subjected to hydrothermal curing for 60 hours and then formed under identical conditions in H₂SO₄ (1.05 sp.gr.) employing 2 A (C/4.5 rate) current for 18 h. Test cells have been assembled with two positive electrodes of dimensions (140 mm(L) × 120 mm (B) × 2.1 mm(T)) and a thinner negative test electrode of dimensions (140 mm × 120 mm × 1.9 mm) in between the positive electrodes. The positive electrode paste mix consisted of 99.9% of leady oxide and 0.1% of Dynle fiber.

The initial capacity of the test cells was about 9 Ah. The electrodes were separated by a polyethylene separator (150 mm × 135 mm × 0.9 mm). The assembled electrodes were immersed in standard accumulator cases of dimensions (170 mm × 180 mm × 50 mm) with an excess of sulfuric acid of 1.28 sp.gr. (without any mechanical pressure) along with packing separators.

The cells were subjected to regular charge/discharge cycling at room temperature (25 °C), performed at a C/5 charge rate and C/5 discharge rate.

SEM images have been recorded for small size pieces (0.5 cm × 0.5 cm) taken from the negative electrodes of the test cells at the completion of 25 charge/discharge cycles.

3. Results and discussion

HRTEM images recorded for the as received MWNT and graphene materials are shown in Fig. 1(a) and (d). The impure particles present in these materials have been analyzed with Energy Dispersive Spectroscopy (EDS). EDS analysis showed that the MWNT material contained Fe, Mg, and Mo metal impurities (Fe: 0.96 wt%, Mg: 1.98 wt %, and Mo: 2.55 wt%). Graphene material contained Fe, Co, Mg and Ca metal impurities (Fe: 0.92 wt%, Co: 4.91 wt%, Mg: 10.89 wt%, and Ca: 0.28 wt%). Both MWNT and graphene materials were purified as mentioned earlier. HRTEM images have been recorded and they are shown in Fig. 1(b), 1(c) and 1(e). Fig. 1(b), 1(c) and 1(d) suggest that the diameter of MWNT is ~ 10 nm and that some impurity metal particles remain as encapsulated deposits during the preparation of MWNT and graphene. Leaching out all the metal particles is not possible. Fewer metal particles only are seen in the purified

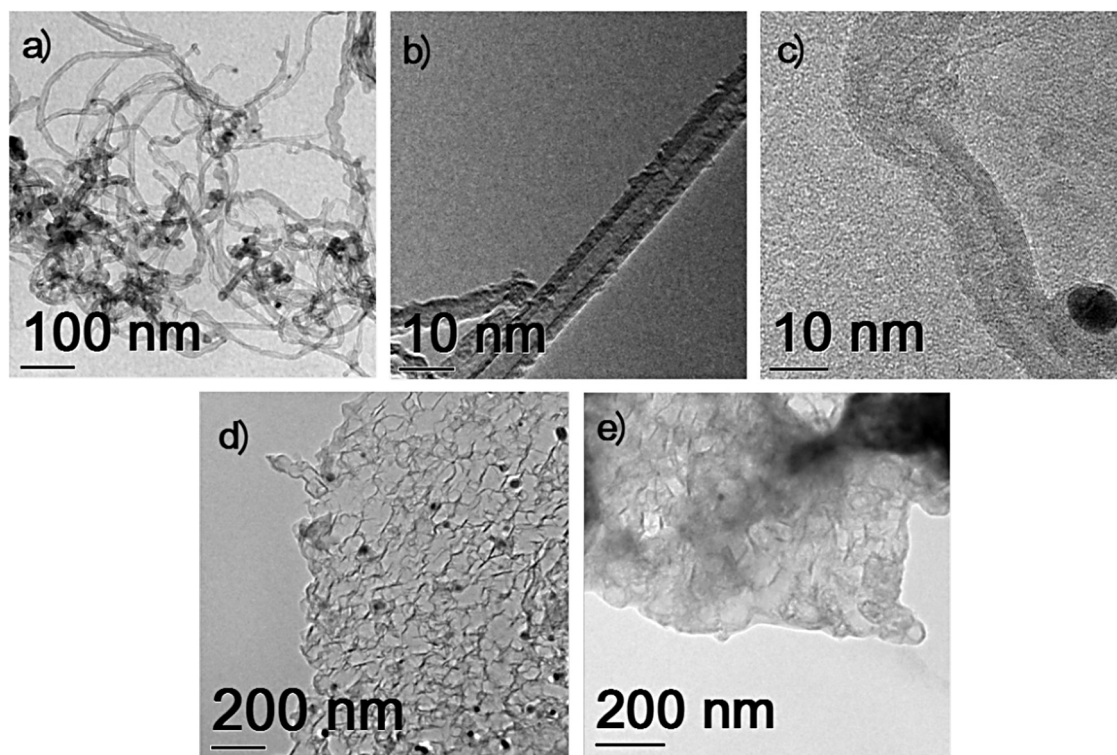


Fig. 1. HRTEM images for the MWNT (a) before and (b and c) after chemical treatment and for the graphene (d) before and (e) after chemical treatment.

materials. For further analyzing the composition of impurity metals, both purified MWNT and graphene have been oxidized in air at 1000 °C and the quantities of the residuals (metals or metal oxides) have been weighed. The quantities of residuals were found to be 0.25 wt% for MWNT and 0.2 wt% for graphene. Presence of low quantities of impurities does not accelerate hydrogen and oxygen gases evolution when these nanostructured carbon materials are introduced in the NAM of the lead acid battery negative electrodes as additive materials. In a later section of this manuscript, we have pointed out that the electrodes prepared in our laboratory by incorporating some additive materials do not evolve hydrogen and oxygen gases during charge/discharge cycles.

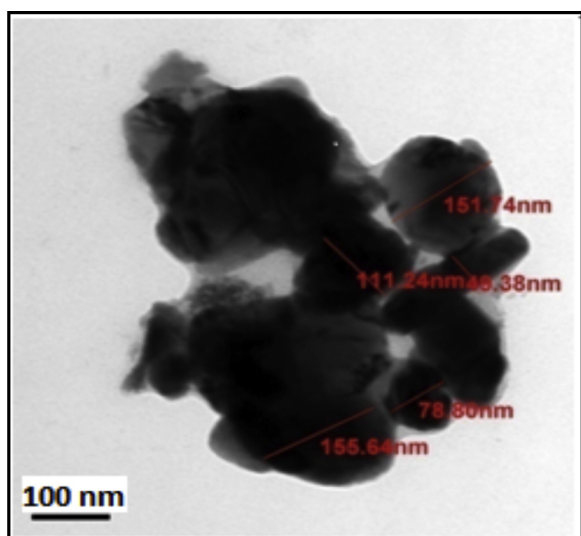


Fig. 2. HRTEM image recorded for the leady oxide.

The HRTEM images recorded for the Vulcan XC 72 indicated that the carbon particles are having spherical shape and the average diameter of the carbon particle is 45 nm.

Fig. 2 shows the HRTEM image recorded for the leady oxide that was used as the starting material for preparing the negative paste mix of the present study. It indicates that the oxide particles are having more or less spherical shape and the average diameter of the particles is 109 nm.

The XRD pattern recorded for the synthesized lead oxide particles have been found to match with the reported data for α -PbO₂ material (JCPDS Card No. 72-2440). Hence, it is concluded that the synthesized lead oxide material is α -PbO₂. The HRTEM image recorded for this is shown in Fig. 3 and it suggests that the α -PbO₂ is formed as nanorods. The average length and diameter of these rods are 1005 nm and 68 nm, respectively.

The XRD pattern recorded for the ball milled lead oxide particles have been found to match with the reported data for α -PbO material (JCPDS Card No. 65-1471). The HRTEM recorded for this α -PbO is shown in Fig. 4 and it suggests that α -PbO is formed as nanospheres with varying diameters ranging from 2 nm to 25 nm.

The charge-discharge curves (fifth cycle) for the test cells incorporated with the carbon additives are shown in Fig. 5(a) and those for the lead oxide additives are shown in Fig. 5(b). The data obtained for the electrodes without additive inclusion are also shown in both figures for comparison. Improved performances are noticed for all the additives incorporated electrodes both during charging and discharging processes. Comparison of discharge curves indicate that the specific capacity of the negative electrodes increase on incorporating various additives into their active materials which in turn suggest that the a.m.u of the negative electrodes increases with the addition of nanomaterial additives.

The a.m.u values were calculated from the specific capacity values for different additives added negative electrodes using the relationship:

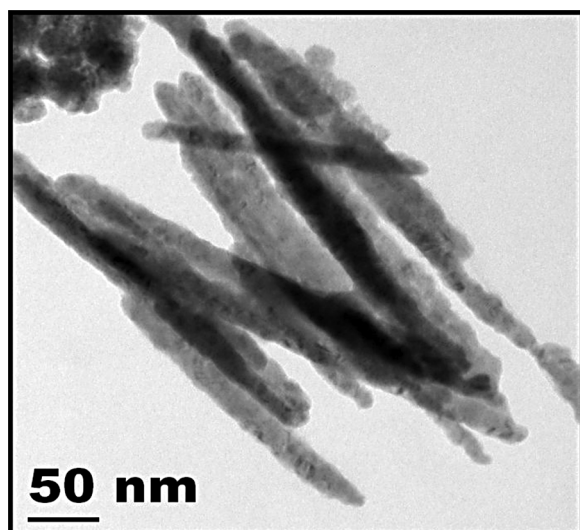


Fig. 3. HRTEM image for the synthesized α -PbO₂.

a.m.u

Discharge capacity at voltage 1.95V

$$= \frac{\text{Theoretical capacity of Pb available in the negative paste mix} \times 100}{\text{Discharge capacity at voltage 1.95V}}$$

The a.m.u values for different additives added negative electrodes are shown in Table 2. The maximum specific capacity and a.m.u have been noticed for the MWNT incorporated negative electrodes. The order of increase in capacity and a.m.u are as follows: MWNT > graphene > Vulcan carbon > lead oxide nanorods > fullerene > ball milled oxide nanospheres > no additive. It is interesting to note that the graphene and the MWNT, the carbon allotropes additives with higher aspect ratios, give 11% and 12% higher capacity and higher a.m.u, respectively, than those of the electrodes without additive. Ball milled lead oxide nano sphere, fullerene, lead oxide nanorods and Vulcan XC 72 carbon give only 1%, 1%, 5% and 6% higher capacities and active material utilizations respectively.

End of charge potential is observed to be lower for the MWNT, graphene, fullerene, synthesized lead oxide nanorods and ball milled lead oxide nanospheres additives; they do not evolve hydrogen and oxygen gas during cycling. The negative electrodes

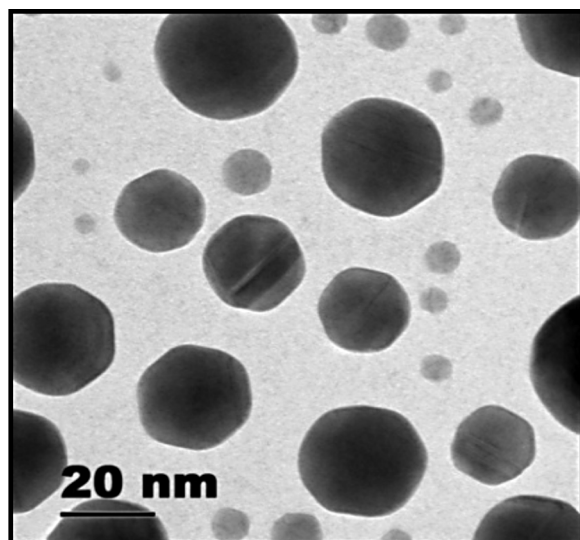


Fig. 4. HRTEM image for the ball milled product α -PbO.

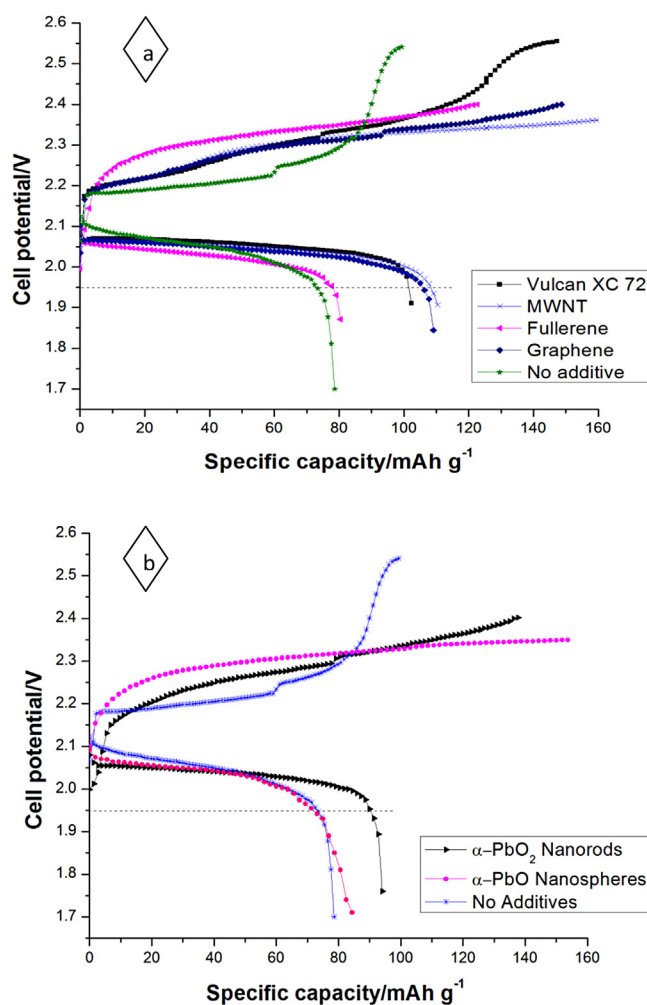


Fig. 5. The charge-discharge curves (fifth cycle) for the test cells incorporated with various nanostructured materials. The details of Fig. 5(a) and 5(b) are mentioned in the insets.

with no additive and with Vulcan XC 72 carbon active additive have strong effects for gas evolution.

It has been mentioned [1–6] that the general cause for the observation of low a.m.u and low specific capacity of negative plates is due to the progressive accumulation of lead sulphate on the structure of the plate with cycling; PbSO₄ crystal size accumulates up to 20 μ m size when additives are not included [7]. Crystal size up to 5 μ m is noticed in our negative electrodes in which no additives have been added. Fernandez et al. [14] have pointed out that lead sulphate tends to accumulate on the outer part of the plate, forming a strong and dense layer that heavily inhibit the acid diffusion to the reaction pores, as well as creating a high ohmic resistance barrier as PbSO₄ is an insulating material. This fact originates strong ohmic drop and polarization effects due to acid depletion or overconcentration and they strongly reduce the charge and discharge performances. In order to reduce the ohmic drop and to increase the conductivity, various groups have tried including various carbon materials possessing different surface area. It is conceivable that carbon particles might provide an electronically conducting pathway through PbSO₄ crystal regions. However, it has been observed that different types of carbon give rise to vastly different results when added incrementally to the negative active mass [10,21]. Some types of carbon gave excellent protection against negative plate sulfation, while others appeared to provide virtually none. Therefore, it has been

Table 2
Active material utilization values

S. No	Without additives	Ball milled oxide nanospheres	Fullerene	Lead oxide nanorods	Vulcan carbon XC 72	Graphene	MWNT
1	31%	32%	32%	36%	38%	42%	43%

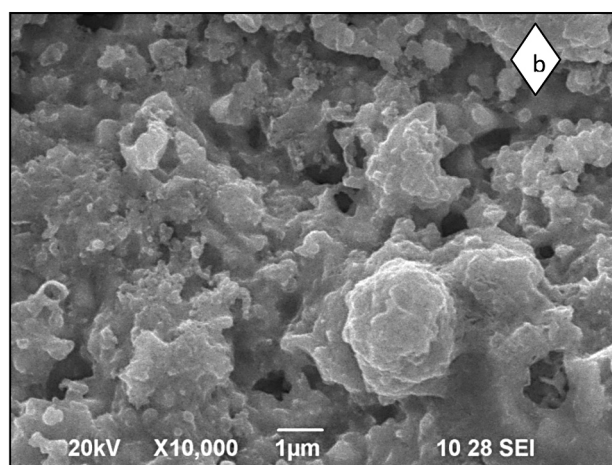
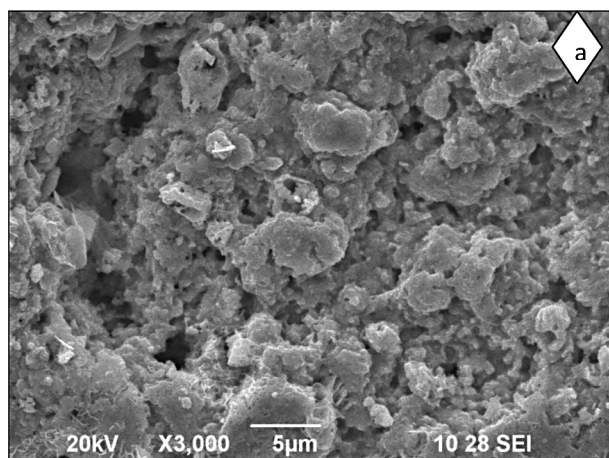


Fig. 6. (a) and 6(b). SEM images for the negative electrode without any additive materials under different magnifications.

suggested [12] that other processes might also be playing a role, apart from the conductivity contribution. It was proposed that the carbon might control the growth of lead sulfate crystals [10] and carbon with lesser particle size (high surface area) could be particularly beneficial. As expected, Pavlov et al. [11,12] observed that the sizes of sulphate crystals decreased from large size ($\approx 10 \mu\text{m}$) to smaller size ($\approx 0.5 \mu\text{m}$) when the size of the additive carbon was decreased from μm level to nm level. Calabek et al. [7] observed $\approx 10 \mu\text{m}$ sized sulphate crystals while adding a graphite additive having particle size $4 \mu\text{m}$. Pavlov et al. [11,12] also reported that when carbon black particles of nano-sizes (i.e. much smaller than the diameter of the NAM skeleton branches) were used, the carbon particles were incorporated into the bulk of the lead skeleton branches of the NAM. The shapes of the crystals as observed through SEM by them were irregular.

The SEM micrographs have been recorded for gathering morphological information on our negative electrodes containing highly performing MWNT and graphene additives. The micrographs have also been recorded for the electrodes without any additive and for the Vulcan XC 72 carbon added electrodes to understand the microstructure differences. Micrographs were recorded on the

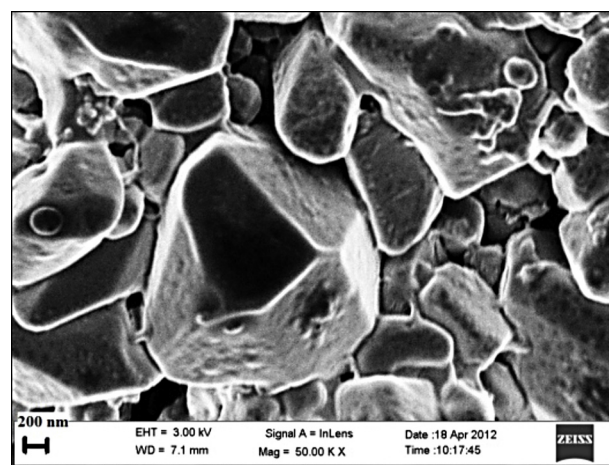


Fig. 7. SEM for the Vulcan XC 72 carbon added present negative electrode.

surfaces of the negative electrodes in the discharged condition at the completion of 25 charge/discharge cycles.

The micrographs recorded for the present electrodes without any additives under 2 different magnifications are shown in Fig. 6. Despite recording the micrographs at two different magnifications at two different locations, single information is only obtained i.e. presence of irregularly shaped PbSO_4 crystals in the size range from $1 \mu\text{m}$ to $5 \mu\text{m}$ is observed. The micrograph recorded for the present Vulcan XC 72 carbon (the average particle size is 45 nm) added electrodes, Fig. 7, also shows presence of irregularly shaped crystals but in the $1 \mu\text{m}$ range. The carbon particles are incorporated into the bulk of the lead sulphate crystals.

It appears that when nanostructured MWNT and graphene (dimensions of both materials are smaller than that of Vulcan carbon XC 72) are introduced as additives in the NAM, the additive particles get integrated into the skeleton structure of the negative plates and the resulting PbSO_4 crystals possesses strikingly different and uniform rectangular bead shapes whose sizes are lesser than 200 nm , Fig. 8 (a) and 8(b). The changes in porosity in these negative electrodes have been measured by liquid (glycerol) adsorption method. The porosity estimated from the glycerol adsorption method for the MWNT and graphene added electrodes are 36% and 34%, whereas that of the electrodes without additive is only 17%. Small bead crystals have created larger pore volumes within the negative plates which could possibly improve acid movements. Under these circumstances, the grid/active material interface is greatly enhanced and consequently electron transport between the grid and the active material is also enhanced. This helps to catalyze the negative electrode reaction ($\text{PbSO}_4 \rightarrow \text{Pb}$) efficiently and increase its reaction rate.

Since maximum improved specific capacity (12%) and pore volume (36%) have been noticed for the MWNT additive in this study, a laboratory level experiment for following the change in specific discharge capacities with cycling has been carried out on the negative electrode containing only MWNT additive and compared with control.

Fig. 9 shows the change of specific discharge capacities for the MWNT added and no additive added test cells during the cycling test. No deterioration in the performance is noticed for the cells

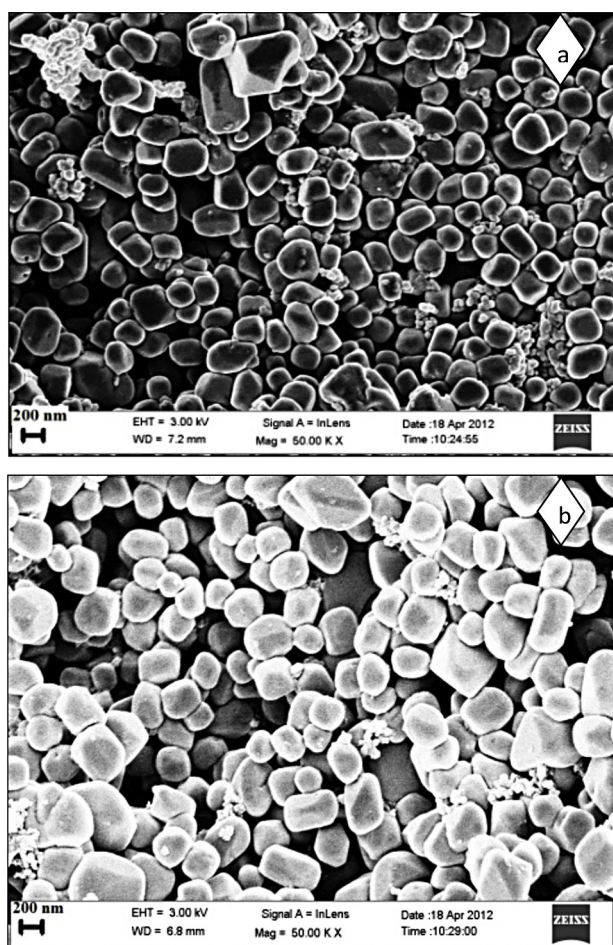


Fig. 8. SEM micrographs for (a) MWNT added negative electrode and (b) graphene added negative electrode.

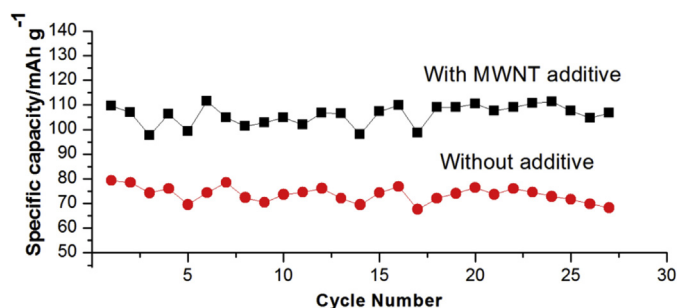


Fig. 9. Comparison of cycle life data for the test cells with and without the MWNT additive.

with the MWNT addition during 27 cycling whereas slight deterioration in the performance is noticed for the cell without additive. This demonstrates the positive effects brought out by the nanomaterial additive.

At the time of completing the write up of this manuscript, we came across a report by Saravanan et al. [22] claiming an observation of increase in capacity and cycling performances on adding the MWNT to the NAM of a laboratory level electrode of size 45 mm × 50 mm × 1.2 mm. This observation on the laboratory level electrode is along the same line as what we have observed for our large size electrodes.

5. Conclusions

Comparison of charge/discharge performances of various additives added large size negative plates suggests that the specific capacity and the active material utilization values improve in the order MWNT > graphene > Vulcan carbon > lead oxide nanorods > fullerene > ball milled oxide nanospheres > no additive. The micrographs of the MWNT and graphene added electrodes show the presence of particles possessing uniform rectangular bead morphology with size lesser than 200 nm. This happens because these additive particles get integrated into the skeleton structure of the negative active material. These bead crystals have also created larger pore volumes within the negative plates and hence acid movements will also be improved. Under these circumstances, the grid/active material interface is greatly enhanced and consequently electron transport between the grid and the active material is also enhanced. This helps to catalyze the negative electrode reaction efficiently and increase its reaction rate i.e., the lead sulphate crystallites are converted to Pb more easily. The idea of adding CNT/graphene as additive materials in the Pb acid battery electrodes appears to yield fruitful results. It could further be exploited and maximum benefit could be derived out of it while designing the lead acid batteries for future applications. Also, for applications such as in hybrid electric vehicles, partial state of charge tests should be carried out before these nanostructured materials are incorporated into the negative plates of the lead acid batteries.

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